

Impact of Microorganisms on Arsenic Geochemistry

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Introduction

Microbial activities are ubiquitous in the geochemical environment, and they can exert tremendous influences on the biogeochemical cycles of elements by interconverting species that display remarkably different behaviors. Arsenic is one such element, possessing a multi-dimensional biogeochemical cycle with important components contributed both directly, by microbial transformations of arsenic itself, and indirectly, by microbial transformations of elements with biogeochemical cycles that intersect that of arsenic.

Microbial Energy Generation by Catalyzing Redox Reactions

One of the primary tasks of a microorganism is to catalyze chemical reactions that will help it to obtain energy for metabolic growth from its environment, and as a result, many of the biogeochemically significant transformations that microorganisms catalyze are the result of energy-generating endeavors. The greatest energy-generating reactions available to the biosphere are those in which electrons are transferred from one element or compound to another, also known as oxidation-reduction or “redox” reactions (39). Redox reactions necessarily alter the electronic configurations of the compounds involved, and because electronic associations form the basis for much chemical reactivity, redox reactions frequently create dramatic alterations in the behaviors of their substrates (33). In addition, because the microbial incentive to catalyze energy-generating reactions is so great, and because the abiotic rates of redox reactions are frequently so slow, such reactions frequently proceed much more rapidly and to a much greater extent in the presence of microbial catalysis than they would otherwise (21).

Aerobic and Anaerobic Respiration

Microorganisms catalyze redox reactions by means of “respiratory” processes, which are those that catalyze the transfer of electrons from one reactant to another. Aerobic respirations couple the oxidation of an electron donor such as organic carbon, H_2 , or $Fe(II)$ to the reduction of molecular oxygen, O_2 , forming water. These processes necessarily occur in unsaturated soils or well-mixed or oligotrophic surface waters where oxygen is abundant (7). In contrast, anaerobic respirations couple the oxidation of an electron donor to the reduction of an alternative electron acceptor such as nitrate, $Fe(III)$, or sulfate, generating N_2 , $Fe(II)$, or sulfide, for example (44). Aerobic and anaerobic respiratory processes form one central class of processes that strongly influence arsenic biogeochemistry, both directly and indirectly.

Respiratory Arsenic Transformations

Within the past seven years, microorganisms have been discovered in a great diversity of anoxic environments that are able to generate energy by coupling the oxidation of H_2 or organic carbon to the reduction of inorganic $As(V)$, arsenate, forming inorganic $As(III)$, arsenite (3, 10, 11, 15, 17, 23, 24). Arsenite behaves much differently than arsenate in natural environments; in particular, its sorption onto clay minerals and metal oxides appears to be less rapid and/or less stable, with the result that $As(III)$ is generally much more mobile than $As(V)$ in aqueous systems (1, 14, 18, 19, 25, 35, 36, 38).

Because arsenate reduction is an energy-generating process for the microorganisms involved, and because arsenite is both more toxic and more mobile than arsenate, this process has the potential to influence greatly the geochemistry of arsenic in anoxic systems, particularly with respect to arsenic mobilization (2, 10). The converse respiratory process, the oxidation of arsenite to arsenate, coupled to the reduction of O_2 to water, has the theoretical potential to generate energy for microbial growth, but has been indicated in only one microorganism to date (12). Nevertheless, a variety of other microorganisms have been shown to oxidize arsenite to arsenate by non-energy-generating mechanisms (26, 27, 34, 41).

Respiratory Iron, Manganese, and Sulfur Transformations

Sorption onto iron and manganese oxide solids, and precipitation in sulfide solids in anoxic environments, appear to be the two primary mechanisms governing arsenic mobility in aqueous, soil, and sedimentary environments (6, 30). Consequently, microbial activities that affect the abundances of iron or manganese oxides or sulfides have indirect, but potentially very important, influences on arsenic geochemistry. Respiratory iron and manganese reduction are ubiquitous and, in many cases, dominant redox processes in anoxic soils and sediments (16, 22). Because the reduced forms of iron and manganese are highly soluble, their oxides dissolve readily upon microbial reduction, simultaneously releasing sorbed substances such as arsenic (10). When sufficient sulfate is present in an anoxic region, however, microbial sulfate reduction can potentially generate sufficient sulfide to precipitate the arsenic in solids such as amorphous arsenic sulfide, realgar, or orpiment (20). The corresponding oxidative processes, microbial oxidation of Fe(II), Mn(II), or S(-II), are known to occur, but are usually restricted to acidic environments (32) and have not been shown directly to promote arsenic sorption onto metal oxides nor to promote arsenic sulfide dissolution. While the geochemical significance of the reductive processes for arsenic cycling is well-established, the significance of the oxidative pathways is much less understood.

Arsenic Toxicity

In addition to energy generation, a second important task for microorganisms is to protect themselves from toxic substances. Arsenate, with its structural similarity to phosphate, enters microbial cells readily through phosphate-uptake proteins. Its primary mode of toxicity is then to displace phosphate in the production of adenosine triphosphate (ATP), the primary energy currency of the cell. The resulting molecules hydrolyze spontaneously, causing the cell to deplete its energy stores rapidly (43). Although this mechanism of toxicity is quite effective, many cells are able to induce highly phosphate-specific uptake proteins that improve the exclusion of arsenate (29, 40, 42). Arsenite, in contrast, is uncharged at neutral pH and appears to gain access to the cytoplasm by less specific mechanisms, possibly including diffusion across the membrane. Once inside, it crosslinks sulfhydryl groups on enzymes, forming stable adducts that permanently disable the enzyme. This mechanism is even more destructive to the cell than that of arsenate (43).

Arsenic Detoxification

To protect themselves against the toxic effects of arsenic, many microorganisms have evolved strategies for detoxification. The best-studied among these is the microbial reduction of arsenate to arsenite by means of the *Ars* system, an enzymatic process in which energy is actually consumed to drive the reduction. The *Ars* system is borne on plasmids that are easily transferred among both Gram-positive and Gram-negative bacteria, and it is induced at arsenic concentrations low enough to be relevant to contaminated environments, with the result that this process is potentially rapid, extensive, and ubiquitous in both oxic and anoxic environments (13, 37).

Certain other bacteria and fungi appear to detoxify arsenicals by reducing them to arsine, As(-III), in both inorganic and methylated forms (8, 9). In addition, some algae have been shown to reduce arsenate to arsenite, presumably for detoxification purposes, but this purpose has not been confirmed (31). Finally, certain bacteria and algae, as well as many higher organisms, may incorporate arsenic into organic compounds such as arsenocholine, arsenobetaine, and other arsenosugars (4, 9). Regardless of the utility to the microorganism, however, it is clear that many non-energy-generating microbial transformations of arsenic occur both rapidly and extensively in natural environments, and should be considered potentially important contributors to arsenic geochemistry.

Passive Nucleation

Microbial cell surfaces possess an abundance of surface functional groups that can form complexes with dissolved ions, including arsenic oxyanions, and such complexes have been shown to function as sites of nucleation in the precipitation of certain minerals (5). In the case of arsenic, it may be possible that microbial cell surfaces contribute to arsenic geochemical cycling in this passive manner as well, particularly in the instance of nucleating arsenic sulfide precipitation (23, 28).

Summary

In oxic environments, the dominant microbial influences on arsenic geochemistry appear to be the bacterial and algal oxidations of arsenite to arsenate, diminishing both toxicity and mobility of the arsenic, as well as confirmed

detoxification processes, including the *Ars*-mediated reduction of arsenate to arsenite and fungal generation of arsines. In anoxic environments, in contrast, the dominant microbial roles are expected to be the respiratory reductions of arsenate, iron, and manganese, all of which promote arsenic desorption and enhance its mobility, and the respiratory reduction of sulfate, which promotes arsenic immobilization into sulfide solids. While the mechanisms underlying these processes are well-understood in many cases, and their geochemical influences are potentially great, the ability to quantify and, more importantly, to predict the rates and extents of these processes in natural environments, remains a tremendous challenge for the future.

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